

Minerals Formed by Organisms

Heinz A. Lowenstam

In the past two decades our knowledge of the diversity of biomineralization products and processes has increased beyond expectation. The vast array of organisms now known to precipitate minerals, the numerous cell and tissue sites at which they form and reform, and the diverse functions which they fulfill were to a large extent unknown until recent years (1, 2). In this article I attempt to document much of this diversity and, where possible, to begin the task of identifying underlying trends and associations. I emphasize the properties of the

ment. Calcium carbonate buildup has defined the morphology of continental margins over vast areas. By presenting this material, I hope to reemphasize the need for improving our understanding of this important biological process.

Diversity of Biogenic Minerals

A total of 31 different biogenic minerals have been identified to date (2). Figure 1 lists these minerals and shows their distribution in the phyla of the five king-

Summary. Organisms are capable of forming a diverse array of minerals, some of which cannot be formed inorganically in the biosphere. The initial precipitates may differ from the form in which they are finally stabilized, or during development of the organism one mineral may substitute for another. Biogenic minerals commonly have attributes which distinguish them from their inorganic counterparts. They fulfill important biological functions. They have been formed in ever-increasing amounts during the last 600 million years and have radically altered the character of the biosphere.

biogenic minerals themselves and introduce the subject of biomineralization processes, which are generally less familiar.

In the broader context, understanding biomineralization goes beyond the important need to identify the fundamental mechanisms involved. Throughout geological time the formation of minerals by organisms has increasingly modified the chemical and physical nature of the biosphere (3). Aspects of the chemistry of the oceans have been radically changed. Biogenic minerals have contributed significantly to the sedimentary environ-

ments. A nearly threefold increase in the number of identified biomineralization products has occurred since a similar compilation was made 17 years ago (4). In particular, additional phosphates, iron oxides, iron sulfides, and manganese oxides have been discovered (1, 2). We can now discern three dominant traits in biomineralization products: (i) two-thirds are calcium minerals, (ii) almost two-thirds contain H_2O or OH , and (iii) one-fourth consist of colloidal materials (2).

The distribution of biogenic minerals between the five kingdoms shows that 25 are synthesized by animals, 11 by protoctists, 8 by monerans, 7 by vascular plants, and 4 by fungi (2). Animals are thus singled out as the most versatile mineralizers, although this may, in part, be due to the fact that they have been more extensively investigated than the others. The distribution of biogenic minerals within the phyla, as shown in Fig. 1, confirms the long-established fact that carbonate minerals are by far the most

widely utilized bioinorganic constituents. Carbonate minerals such as vaterite, monohydrocalcite, and amorphous calcium carbonate cannot now be considered biological oddities, inasmuch as they are found in species of many genera (Fig. 1). Opal emerges as the second most extensively formed biogenic mineral. Ferrihydrite and related ferric oxide minerals rank third, and magnetite (Fe_3O_4), first discovered as a biomineralization product in chiton teeth (5) and now known to be synthesized by magnetotactic bacteria (6, 7), honey bees (8), and homing pigeons (9), may well prove to be the fourth most extensively formed biogenic mineral.

Mineral-Forming Processes

Two fundamentally different processes of mineral formation can be distinguished. The first, exemplified by numerous animals, is an "organic matrix-mediated" process. In general, the organism constructs an organic framework or mold into which the appropriate ions are actively introduced and then induced to crystallize and grow. The mineral type, orientation of crystallographic axes, and microarchitectures are under genetic control.

The second basic process of mineral formation, exemplified by some bacterial species as well as various green and brown algae, is characterized by bulk extracellular and/or intercellular mineral formation, without the elaboration of organic matrices. This "biologically induced" mineralization results in the minerals having crystal habits similar to those produced by precipitation from inorganic solutions. Resulting polycrystalline aggregates—found, for example, in the intercellular spaces of some green algae—show random orientation of their mineral constituents (10). The bacterial mineral precipitates form as a result of the interaction between the biogenically formed gases and metal ions present in the external medium (11). In the algae, mineral formation results from the reduction of CO_2 in the external medium due to photosynthetic activity. As the water in which these algae live is generally supersaturated with respect to calcium carbonate, the CO_2 reduction induces the minerals to form (12). These biologically induced mineral-forming processes are far less rigorously controlled than organic matrix-mediated mineralization, and they appear to constitute an earlier, more "primitive" stage in the evolution of biogenic mineral formation.

The author is a professor of paleoecology in the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena 91125. This article is based in part on a talk presented at the Conference on Advances in the Biogeochemistry of Amino Acids held 29 October to 1 November 1978 at Airlie House, Warrenton, Virginia. The conference was jointly sponsored by the Carnegie Institution of Washington and the National Science Foundation and marked the 25th anniversary of Philip H. Abelson's discovery of amino acids in fossils and the occasion of his retirement as president of the Carnegie Institution of Washington. Parts of the talk have been published in *Biogeochemistry of Amino Acids*, P. E. Hare, T. C. Hoering, K. King, Jr., Eds. (Wiley, New York, 1980).

Structural Complexity and Sites of Deposition

Biogenic minerals may be amorphous, paracrystalline, or crystalline (2). At a given site, they may occur as a single unit (such as a single crystal), numerous individual units, or aggregates. The latter, in turn, are known to form structures of varying degrees of complexity. Mineralized skeletal hard parts are examples of such aggregates. The aggregated units are usually arranged in an orderly fashion, and when crystalline, the crystallographic axes are partially or fully aligned (13, 14). These ordered structures are generally differentiated into a number of microarchitectural units, each of which is enveloped by an organic ma-

trix sheath (Fig. 2a) (15). Compound aggregates with randomly oriented crystallographic axes, such as are found in some algae (Fig. 2b), are less common. In exoskeletal structures an additional organic veneer may protect the mineralized hard parts from the external environment. The organic matrix structural framework and the surficial organic veneers appear to be absent in aggregates with randomly oriented mineral constituents, such as some green algae. The structural complexity of biogenic minerals, ranging from single crystals to compound aggregates, can be conveniently subdivided into six categories (2).

Mineral deposits are formed either intracellularly, intercellularly, or extracellularly (16). The intracellular mineral-

ization site is by far the most common. It occurs in a few monerans (bacteria) and is abundant in three of the four eukaryotic kingdoms (Protoctista, Animalia, and Plantae). Intracellular deposits are located within organelles or in vesicles. The most commonly identified sites are the mitochondria, the Golgi complex, or vesicles, which are intimately associated with the latter. Intercellular mineralization occurs in some multicellular filamentous algae, but is not, as yet, known in plants or animals. Extracellular mineralization sites are widespread and well known from all five kingdoms.

Monerans, most protoctists, and fungi have only one mineralized site, which may be intra-, inter-, or extracellular. In

KINGDOM	PHYLUM	MONERA										PROTOCTISTA										FUNGI		ANIMALIA										PLANTAE													
												DINOFLAGELLATA	HAPTOPHYTA	BACILLARIOPHYTA	PHAEOPHYTA	RHODOPHYTA	CHLOROPHYTA	ZYGEMATOPHYTA	RHIZOPODEA	SIPHONOPHYTA	CHAROPHYTA	HELIOTROCHA	RADIOLARIA	FORAMINIFERA	MIXOMYCOTA	CILIOPHORA	BASIDIOMYCOTA	DEUTEROMYCOTA	PORIFERA	COELENTERATA	PLATYHELMINTHES	ECTOPROCTA	BRACHIOPODA	ANNELIDA	MOLLUSCA	ARTHROPODA	SIPUNCULA	ECHINODERMATA	CHORDATA	BRYOPHYTA	TRACHEOPHYTA						
CARBONATES:																																															
	CALCITE	+	+	+																																											
	ARAGONITE	+		?		+	+	+																																							
	VATERITE																																														
	MONOHYDROCALCITE	+																																													
	AMORPH. HYDR. CARB.																																														
PHOSPHATES:																																															
	DAHLITE	+																																													
	FRANCOLITE																																														
	Co ₃ Mg ₃ (PO ₄) ₄																																														
	BRUSHITE																																														
	AMORPH. DAHLITE PRECURSOR																																														
	AMORPH. BRUSHITE PRECURSOR																																														
	AMORPH. WHITLOCKITE PRECURSOR																																														
	AMORPH. HYDR. FERRIC PHOSPHATE																																														
HALIDES:																																															
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	AMORPH. FLUORITE PRECURSOR																																														
OXALATES:																																															
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	WEDDELITE																																														
SULFATES:																																															
	GYPSUM																																														
	CELESTITE																																														
	BARITE																																														
SILICA:																																															
	OPAL																																														
Fe-OXIDES:																																															
	MAGNETITE	+																																													
	MAGHEMITE	?																																													
	GOETHITE																																														

Fig. 1. Diversity and phylum distribution of biomineralization products in extant organisms.

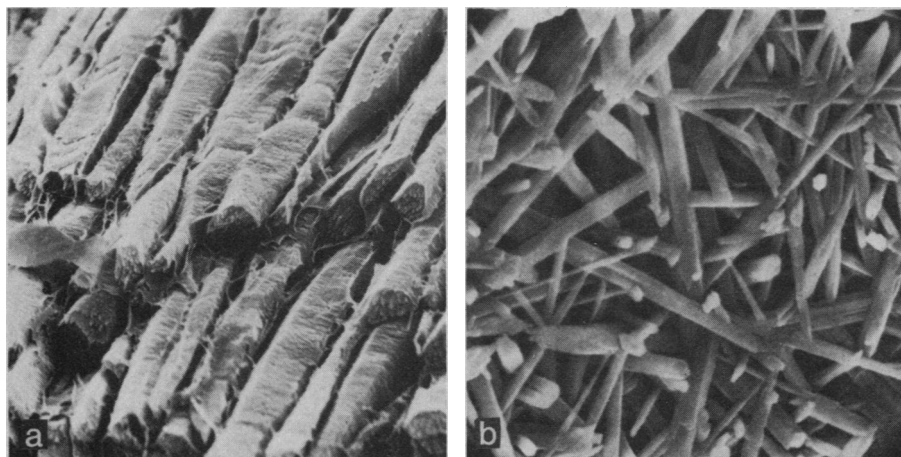


Fig. 2. (a) Example of organic matrix-mediated biomineralization process: calcitic prismatic layer of the bivalve *Mytilus californianus*, showing crystal enveloping organic matrix. (b) Example of biologically induced mineralization process: intercellular array of randomly oriented aragonite crystals in the algae *Galaxaura obtusata*.

many tissue-grade eukaryotes, minerals form at all three sites. Coelomate animals show the greatest diversity in mineral deposition sites. Many of these contain intracellular minerals at a number of tissue localities, and in some cases the intracellular deposits are monomineralic whereas the extracellular deposits may contain a few different mineral types. These are usually located in separate discrete microarchitectural units.

Minerals formed at a particular site may be (i) retained in place, (ii) transferred intact to other sites, (iii) excreted, (iv) dissolved and replaced continuously, periodically, or only occasionally, or (v) continuously reconstituted. Mineral deposits which are subject to dissolution and replacement function, in part, as reservoirs for cations or anions to be used for a variety of vital functions. Transfer of ions destined for mineral formation may involve a single or a multistep dissolution-precipitation process. At the terminal deposition site, the mineral either is stabilized or undergoes continuous reconstitution.

Examples of Biomineralization Processes

The following examples of biomineralization processes both illustrate the various properties described above and are not generally familiar. Magnetotactic bacteria contain intracellular chains of single magnetite (Fe_3O_4) crystals which are bound to the membrane. An as yet unidentified ferric iron oxide-bearing compound may be the precursor of the magnetite crystals (7). The magnetite crystals are stabilized in place by an elongated sheath of organic material.

The swimming behavior of these bacteria in a magnetic field indicates that the magnetite serves as a biomagnetic compass (17). In the planktonic Coccolithophoridae, the calcitic platelets are formed intracellularly in the Golgi cisternae and, upon completion, are extruded to the cell surface (18). The gastropod *Pomacea paludosa* has an aragonitic shell. It forms egg capsules containing vaterite, another polymorph of calcium carbonate. The sources of calcium and carbonate for the shell are amorphous calcium carbonate or vaterite granules, located in the Golgi apparatus of the mantle epithelial cells. It has been suggested that granules localized in the foot, which are composed of amorphous CaCO_3 and trace amounts of vaterite, are used for large-scale sudden mobilization of calcium during shell regeneration. Normally these granules serve as a reservoir for the calcium that regulates muscle activity in the foot. Yet a third reservoir of calcium is located in the albumen-capsule gland of the females. These granules of vaterite provide calcium for mineralization of the egg capsules (19).

Perhaps one of the most complex sequences of mineralization known involves the formation of magnetite crystals in the tooth denticles of a group of mollusks called chitons (20). Iron is extracted from the food and transported in the bloodstream, apparently in the form of a ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) (21) core surrounded by the protein apoferritin (20, 22). The iron from the complex (ferritin) is removed from the blood (23) to the superior epithelial cells of the radula, which adhere tightly to the tooth denticles. These cells accumulate large concentrations of ferritin, which is the stor-

age site for the iron mineralization of the tooth. From here the iron is transferred into the preformed organic matrix framework of the teeth (20, 24). As there is no evidence of intact transfer of ferritin to the tooth denticles, the iron must be transported in the soluble ferrous form across the cell membrane. In fact, the ferritin micelles are observed to be in various stages of demineralization (20). The iron is then redeposited in specific areas on the surface of the tooth in the form of ferrihydrite. Within 1 or 2 days, however, the ferrihydrite is converted to magnetite, by an as yet undetermined biochemical process (24). The unmineralized portions of the organic matrix are later infilled by other minerals such as amorphous hydrous ferric phosphate (5) or lepidocrocite and francolite (25). The hardness of the magnetite affords the chitons an advantage over other grazers by enabling them to recover the algae embedded within the rocks (5). Mineralized hard parts can have a number of functions other than structural and mechanical ones. It is well known that the endoskeletons of mammals act as a reservoir of calcium and phosphorus and are intimately linked to the organism's metabolism. It is perhaps less widely appreciated that many cold-blooded vertebrates as well as invertebrates utilize their hard parts for a similar purpose. In the gastropod genera *Conus* and *Cypraea*, the surface-exposed aragonitic shell walls are always significantly thicker than the inner shell walls. The inner shell wall calcium carbonate is dissolved and transferred, in solution, to the growing shell edge. This process continues throughout postlarval development (26). Other gastropods limit their recycling activity to modify their aperture-restricting ornamentations (27, 28). It has been observed that these species also deposit new shell in a discontinuous manner. Shoal-water bivalves, which are forced to keep their valves closed for extended periods due to storms or unusual tides, are known to "etch" the internal surfaces of their shells. The mobilized carbonate buffers the enclosed fluids and prevents the pH from dropping due to the production of metabolic CO_2 and organic acids (29). Another example of ion mobilization under stress was recently noted in the blue shark, *Prionace glauca*. The aragonitic otoconia (mineralization in the vestibular apparatus) of a pregnant female captured close to the end of gestation showed noticeable surface resorption, suggesting that calcium was mobilized from the otoconia to the rapidly mineralizing embryos (Fig. 3) (1).

In situ Maturation and Ontogenetic Changes

In only a few studies has mineralization been traced in situ from its initiation to the completion of the final product. The iron oxide minerals in chiton teeth illustrate the most radical change noted to date in maturation in situ. Mineralization of the major lateral teeth starts by deposition of ferrihydrite. Transformation to magnetite is initiated within the ferrihydrite deposits and is followed by mass conversion in one tooth row. It continues thereafter on the magnetite surfaces of subsequent tooth rows until the magnetite mineralization phase of the teeth is complete (30).

The mature shells of land and freshwater gastropods are composed of aragonite. However, the newly formed calcium carbonate deposits are reported to be vaterite (31). It is not yet known whether a similar process occurs in marine gastropods. In mammalian bone a number of precursor minerals have been suggested, including amorphous calcium phosphate, tricalcium phosphate, octacalcium phosphate, and brushite (32).

Although many groups of organisms begin to form mineralized hard parts at the embryonic stage, there have been very few studies of these materials. Among them are several that show ontogenetic changes in hard-part mineralogy. In the bivalves studied the larval shell is mineralized by aragonite. In the postlarval shell of *Crassostrea virginica*, however, the mantle-secreted layers contain calcite and the myostracal layers, formed by the cells of the adductor and auxiliary muscles, are mineralized by aragonite (33). Mineralogical changes during ontogeny have also been observed in the pearl oyster *Pinctada* (34). The otoconia in the two auditory chambers of the labyrinth in some sharks show a different mode of mineralogical change during ontogeny (35). Newly formed otoconia of a different mineralogy are added to the initially formed deposits during ontogeny. In the blue shark the otoconia of the embryos are mineralized by amorphous hydrous calcium phosphate (ACP), whereas those formed at the juvenile and adult stages are composed of aragonite (35). Therefore, the otoconia consist entirely of ACP in the embryos, of ACP plus aragonite in the juveniles, and of aragonite with a trace of ACP in the adults. This ACP fraction can be detected only in scanning electron micrographs by its distinct botryoidal surface geometry. In some other species of sharks belonging to the same superorder,

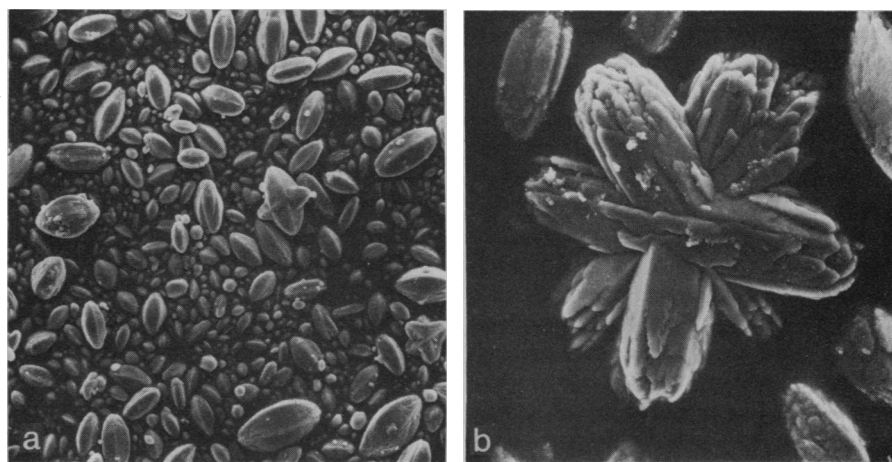


Fig. 3. (a) Aragonitic otoconia from adult shark *Prionace glauca*. (b) Aragonite otoconia from pregnant female of *P. glauca*, showing distinct resorption features.

the otoconia of the embryos are also composed of ACP, whereas the material formed after the embryonic stage is aragonite. In this case, however, the ACP fraction cannot be located in the mature adult otoconia and has apparently been resorbed (32). A most spectacular mode of mineralogical change occurs in the holothurian species *Molpadia intermedia* (36). The mesodermal deposits in early postlarval individuals consist of calcitic spicules, similar to those in other species of this class. During subsequent growth, most spicules outside the oral and caudal regions are either resorbed completely or resorbed and replaced by the minerals amorphous hydrous ferric phosphate and opal. Thus during ontogeny these organisms switch over from calcium carbonate deposition to ferric phosphate and amorphous silica deposition.

Evolutionary Aspects of Biomineralization

Recent discoveries of fossils in Precambrian rocks have extended the documentation of life to about 3500 million years ago (37). Up to late Vendian time (about 600 million years ago), the fossils are all soft-bodied organisms. This had led to the startling realization that mineralized hard-part formation, so widespread in present-day life, is a late development. However, it was certainly preceded by intracellular mineralization and by extracellular biologically induced mineral precipitation by at least 2000 million years. This may be discerned from the $^{34}\text{S}/^{32}\text{S}$ values of many sedimentary pyrites, which show isotopic fractionation similar to that produced by extant sulfate-reducing bacteria (38), and from

the presence of bacteria that are morphologically indistinguishable from extant strains which precipitate manganese oxide minerals (39).

The inception of mineralized hard-part formation enormously enhanced the chance of life being preserved as fossils. It is generally recognized that the rapid spread of this innovation to a wide range of organisms and its continuing proliferation thereafter account for the wealth of biological records preserved during the past 600 million years (the Phanerozoic period). This has enabled paleontologists to define the phylogenies of the groups of organisms that acquired mineralized hard parts, on the basis of morphological changes of skeletal designs and skeletal microarchitectures. Few attempts have been made to extract evolutionary information from the preserved organic constituents of fossils, which may provide insight into underlying processes of biochemical evolution (40).

Few evolutionary changes in the types of minerals formed by organisms during the Phanerozoic can be recognized at present (41). The best documented case occurred at the onset of hard-part mineralization, approximately 600 million years ago (2). Initially, two-thirds of the organisms formed phosphatic (42) and one-third formed calcareous hard parts. Within less than 20 million years (Lower Tommotian) about half the organisms formed calcareous hard parts, and in fact ever since, calcium carbonate polymorphs have proved to be the minerals of choice for most organisms. At the outset calcite was more widely utilized than aragonite.

The anthozoan corals exemplify this trend. The Paleozoic Rugosa had calcitic skeletons, whereas the Scleractinia, which evolved in Triassic time, have

aragonitic skeletons (4, 43). Similar trends may have occurred in the Bryozoa and possibly in the Nautiloidea (13). Thus the fossil record indicates a trend in the evolution of calcareous skeletons from phosphates to carbonates, and within the carbonates a tendency to replace calcite by aragonite.

Impact on the Biosphere

Magnetite is a common mineral formed at elevated temperatures and pressures in igneous and metamorphic rocks. No magnetite is known to be formed inorganically in the biosphere. Yet organisms ranging from bacteria to vertebrates are capable of forming magnetite under atmospheric conditions. The magnetite of chiton teeth is a product of the transformation of a hydrous ferric oxide precursor mineral called ferrihydrite. Even though this is a common product of both biological and inorganic processes in the biosphere, the chitons somehow biochemically mediate this transformation to magnetite even at atmospheric temperatures and pressures.

The mineral fluorite is widely formed at high temperatures in hydrothermal systems and is occasionally found in sedimentary rocks as a result of diagenesis. Like magnetite, it is not formed inorganically in marine or freshwater environments. It, too, is synthesized in the hydrosphere by two groups of organisms (Fig. 1). The statoliths or balancing organs of a wide range of opossum shrimps (Mysidacea), which occupy marine to freshwater environments, contain fluorite (44). Fluorite is also one of the mineralization products of the gizzard plates of the gastropods *Scaphander* and *Meloscapander* (45). The amorphous precursor of this mineral (also not known to be formed inorganically in the hydrosphere) is found in the spicules of certain common marine nudibranch gastropods, where it occurs together with amorphous calcium carbonate (44). Several abundant marine prototists use celestite (SrSO_4) to form their skeletons. As seawater is greatly undersaturated with respect to SrSO_4 , this mineral will certainly not form inorganically, and in fact the skeletons rapidly dissolve after death (46).

One important consequence of the mass production of certain biogenic minerals is that these minerals are prevented from forming inorganically in the hydrosphere. Silica in the form of opal is perhaps the most striking example. No fewer than 10 (possibly 11) different groups of organisms are now known to utilize

opal in forming their hard parts (Fig. 1). The diatoms, silicoflagellates, and radiolarians are primarily responsible for the huge quantities of biogenic opal formed in the oceans. The result is that seawater is undersaturated with respect to opal (3). In their absence, inorganic opal precipitation would take place in the oceans. A less extreme but quantitatively very important example of biogenic mineral formation in undersaturated waters is calcium carbonate in the form of aragonite and calcite. Only the upper portions of the ocean are saturated with respect to calcite and aragonite (47). Organisms, however, synthesize aragonite and calcite at all depths in the oceans, even in the deepest trenches. In all these cases it appears that the organic sheaths that envelop the mineral constituents prevent their dissolution during life (48).

In order to evaluate the impact of the biomineralization process on the biosphere, it is important to be able to distinguish biogenic from inorganically formed minerals. Furthermore, this will improve our ability to recognize biogenic minerals in the sedimentary record and perhaps even allow us to detect extraterrestrial life. In certain cases, the mere presence of the mineral itself is an indication that it is of biogenic origin. Magnetite is an unequivocal example. Biogenic minerals usually adopt characteristic forms defined by the geometry of their organic matrix frameworks. The fluorite crystals in mysid statoliths are always acicular in shape, whereas inorganic precipitates are distinctly different (3). In fact, minute inorganically formed acicular fluorite crystals have only once been observed, in hydrothermal vug fillings (49). Perhaps the most telling difference between biological and inorganically formed minerals is their so-called geochemical properties. Organisms are capable of controlling the trace element and isotopic compositions of the minerals they form, so that these are out of equilibrium with the environment (50). Examples are the strontium and magnesium contents of most mollusk shells (51) and the stable oxygen and carbon isotopic compositions of coral skeletons (52).

Concluding Remarks

The rapid progress made in this field during the past decade or so only emphasizes the fact that much more has yet to be discovered. We have hardly begun to investigate biomineralization processes in the monerans and the fungi. To date, there are only a few well-documented

examples where the initial mineralization deposit differs from the mature form, or where changes in mineral type occur during development. We are now aware that such processes do occur, but we have yet to determine whether they are widespread.

This article demonstrates that the products of biomineralization are unexpectedly diverse. They may be formed, resorbed, modified, or redeposited. The sheer complexity raises the question of whether underlying common strategies have been adopted by different groups of organisms. The widespread use of a pre-constructed organic framework in which the minerals grow is in itself an indication of the existence of a common approach toward biomineralization. Properties of these organic matrices may well provide insights into such basic mechanisms.

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The National Science Foundation Looks to the Future

John B. Slaughter

I wish to address three major topics. First, I want to share with you some recent landmark achievements in fundamental scientific research. At the same time, I hope to show that gathering new knowledge is not only rewarding in itself but represents an investment; the aggregate payoff will surely be great, even though the future applications are sometimes hard to foresee. I will put the case as strongly as I can that continuous and substantial support for basic research is a necessity for all great nations. At the same time, I will assert my own conviction that support of the best research and education in the sciences and engineering is and must remain the central purpose of the National Science Foundation (NSF).

Next, I will take up the role of research that directly addresses some of the pressing needs of our society, such

as energy, natural resources, and productivity. Much of the research that addresses such "real-world" problems is quite fundamental in character. We may call it applied research because we see clearly the problem it addresses, but whether the distinction between basic and applied research represents in every instance a real difference I will leave to your judgment.

Finally, I will turn to two areas that I believe require closer attention and more intense effort in the 1980's. One of these is engineering science, that is, the theoretical body of knowledge and technique underlying the practice of engineering. Much of this work is every bit as fundamental in character as corresponding work in the disciplinary sciences. The other area is education in the science and engineering disciplines. It is apparent that we will face increasing difficulties in

securing talented and well-trained minds for the professional disciplines unless we act promptly to improve our education processes, not only at the university level but in the elementary and secondary schools as well.

Recent Scientific Achievements

In considering major achievements of fundamental scientific inquiry in recent years, I have chosen a handful of examples that I am familiar with because of NSF's involvement or interest in them. I could as easily have chosen many others, equally exciting, if there were space to discuss them. Science is virtually exploding with new developments, and it is a great privilege and responsibility to be rejoining NSF during these heady times.

Certainly a historic advance in our times has been the recent progress toward the theoretical unification of the several forces in nature. Today we have an extremely persuasive conceptual argument, supported by experimental evidence, that the electromagnetic and weak nuclear forces are different expressions of a single phenomenon. Moreover, we sense a possibility that this unification can be extended to the strong nuclear force as well. Gravity—the

The author is director of the National Science Foundation, Washington, D.C. 20550. This article is based on his address at the AAAS Annual Meeting, Toronto, Canada, 3 to 8 January 1981.